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Structure of 3'-5'-dimethyl-6-methoxy 4-2'-benzo[b] furanyl coumarin

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Abstract : The title compound belongs to a family of biheterocyclic benzofuranyl coumarins. The crystal structure has been determined at room temperature using X-ray diffraction intensity data. Plate like colourless crystals are triclinic, spacegroup $P\bar{1}$ with unit cell dimensions a = 7.640(13)Å, b = 9.659(6)Å, c = 11.955(8)Å, α = 85.27(7)° β = 71.74(7)° and γ = 72.72(8)° The structure was solved by direct method and refined by full matrix least squares method to a final R=0.058 for 1836 observed reflections.

Keywords : Oxygenated biheterocyclic benzofuranyl coumarins

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Oxygenated biheterocycles containing coumarin furan and benzofuran moieties have been found to be anti-microbials[1] and anti-inflammatory agents[2]. The title compound was one amongst a series of sterically hindered 4-2'-benzo(b)furanyl coumarins[3]. The spatial proximity of the methyl group on the benzofuran ring and the C3-H of coumarin was demonstrated by 1D difference Nuclear Overhauer Enhancement (NOE) experiments. To further establish the orientation of the two rings the title compound has been subjected to X-ray diffraction studies.

Plate like colourless crystals are obtained with ethanol at room temperature by slow evaporation method. The intensity data has been collected using CAD4 diffractometer using MoKα radiation (λ = 0.7107 Å) [4]. The data has been corrected for absorption by Psi-Scan [5].The crystallographic data are given in Table 1. The structure has been solved by direct method [6] and refined by full matrix least squares method [7] to a final R = 0.058 for 1836 observed reflections.

The fractional coordinates and equivalent isotropic temperature factors for non-H atoms are presented in Table 2.The anisotropic temperature factors for non-hydrogen atoms are

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Table 1. Crystal data for the title compound.

Crystal Morphology	Colourless plate like
Crystal size	0.3 × 0.3 × 0.2mm
Chemical formula	C20 H16 O4
Molecular weight	320.33
Crystal system	Triclinic
Space group	$P\bar{1}$
Cell constants	a = 7.640(13)Å
	b = 9.659(6)Å
	c = 11.955(8)Å
	α = 85.27(7)°
	β = 71.74(7)°
	γ = 72.72(8)°
Volume V	799.9(16)Å^3
Radiation used	MoKα (λ = 0.7107 Å)
Number of formula units z	2
Density (calculated) D_c	1.330gm/cm^3
Density (Measured) D_m	1.288gm/cm^3
Unique data with measured	2804
Observed data with $I \geq 2\sigma(I)$	1836
$F(000)$	336
R	0.058

Table 2. Fractional coordinates and isotropic thermal parameters (A^2) for non-hydrogen atoms with e s d's in parentheses.

Atoms	x	y	z	Uiso
C2	0 7489(4)	-0 4241(3)	0.2838(3)	0 0607(7)
C3	0.7755(4)	-0 3122(3)	0.1996(2)	0.0582(7)
C4	0 6712(4)	-0.1717(3)	0.2215(2)	0 0494(6)
C5	0.3948(4)	0 0065(3)	0.3676(2)	0.0506(6)
C6	0.2561(4)	0 0312(3)	0 4764(2)	0 0541(7)
C7	0 2387(4)	-0 0814(3)	0 5544(2)	0.0647(8)
C8	0.3587(4)	-0 2193(3)	0 5245(2)	0.0636(8)
C9	0.4983(4)	-0 2436(3)	0 4152(2)	0 0549(7)
C10	0 5222(4)	-0 1339(3)	0.3353(2)	0 0471(6)
C2'	0.7062(4)	-0 0641(3)	0 1306(2)	0.0495(6)
C3'	0 7424(3)	-0 0671(3)	0.0119(2)	0 0471(6)
C4'	0 7667(4)	0 1470(3)	-0.1355(2)	0 0525(7)
C5'	0 7544(4)	0 2922(3)	-0.1408(2)	0 0566(7)
C6'	0 7299(4)	0 3658(3)	-0.0377(2)	0 0628(8)
C7'	0.7136(4)	0 2995(3)	0 0699(2)	0 0600(7)
C8'	0 7227(4)	0 1545(3)	0.0715(2)	0.0489(6)
C9'	0.7491(3)	0.0765(3)	-0 0273(2)	0.0470(6)
C11	0 7584(4)	-0 1890(3)	-0 0643(2)	0.0594(7)
C12	0.7652(5)	0 3750(3)	-0.2551(3)	0 0771(9)
C13	0 1308(5)	0 2802(3)	0 4348(3)	0.0802(10)
O1	0.6126(3)	-0.3853(18)	0.3903(16)	0.0640(6)
O2	0.8415(3)	-0.5519(2)	0.2686(19)	0.0800(7)
O3	0 6973(3)	0.0702(18)	0.1700(14)	0.0554(5)
O4	0.1297(3)	0.1644(2)	0 5159(16)	0 0700(6)

presented in Table 3. Table 4 gives selected bond lengths and bond angles. An ORTEP [8] plot of the molecule is as shown in Figure 1. The packing diagram of the molecule down 'a' is as shown in Figure 2.

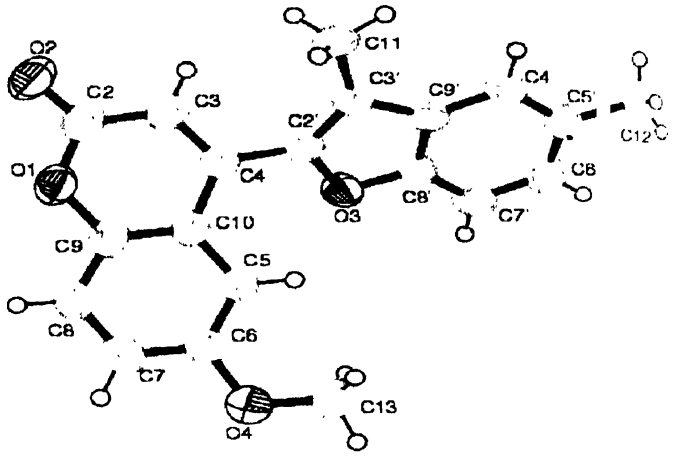

Figure 1. ORTEP diagram 50% thermal ellipsoidal probability

All the C-C and C-H bond lengths in the coumarin and benzofuran rings are characteristic of sp^2 hybridised carbons. However, the higher sp^2 C4-sp^2 C2' bond length of 1.459(4)Å indicates the absence of π-electron delocalization. A slight

Table 3. Anisotropic displacement parameters ($Å^2$) for non -hydrogen atoms with e s.d's in parentheses

Atom	U11	U22	U33	U12	U23	U23
C2	0.0731(2)	0.0462(16)	0 0692(18)	0.0026(13)	-0 0315(16)	-0 0156(14)
C3	0.0596(18)	0.0527(16)	0.0631(16)	0.0002(13)	-0.0238(14)	-0 0114(13)
C4	0 0525(16)	0.0481(15)	0 0533(14)	0 0012(11)	-0 0222(12)	-0 0165(12)
C5	0.0614(17)	0.0464(14)	0.0471(14)	0.0054(11)	-0.0205(12)	-0 0173(12)
C6	0.0599(17)	0.0548(16)	0.0499(15)	-0 0030(12)	-0.0202(13)	-0 0150(13)
C7	0 067(2)	0.0780(2)	0.0495(16)	0 0012(14)	-0 0125(14)	-0.0262(16)
C8	0.081(2)	0.0614(18)	0.0562(16)	0 0132(13)	-0 0221(15)	-0 0333(16)
C9	0 0669(18)	0.0500(15)	0 0569(16)	0 0023(12)	-0.0255(14)	-0.0235(13)
C10	0 0555(16)	0.0466(14)	0.0468(13)	0.0025(11)	-0.0224(12)	-0.0188(12)
C2'	0.0545(16)	0.0456(14)	0 0511(14)	-0.0046(11)	-0.0153(12)	-0.0177(12)
C3'	0.0417(14)	0.0483(14)	0.0498(14)	-0.0064(11)	-0.0126(11)	-0.0103(11)
C4'	0.0526(16)	0.0577(16)	0.0460(14)	-0.0038(11)	-0.0095(12)	-0.0184(12)
C5'	0.0536(17)	0.0581(16)	0 0582(16)	0.0087(12)	-0.0137(12)	-0.0216(13)
C6'	0.0691(19)	0.0475(15)	0.0709(19)	0.0021(13)	-0.0136(15)	-0.0239(14)
C7'	0.0712(19)	0.0535(16)	0 0577(16)	-0.0084(12)	-0 0127(13)	-0.0263(14)
C8'	0.0509(16)	0.0512(15)	0.0468(14)	0 0004(11)	-0.0121(11)	-0.0207(12)
C9'	0.0441(15)	0.0492(15)	0.0466(13)	-0.0031(11)	-0.0111(11)	-0.0136(11)
C11	0.0704(19)	0.0488(15)	0.0572(16)	-0.0103(12)	-0.0198(14)	-0.0112(13)
C12	0.087(2)	0.0790(2)	0.0676(19)	0.0184(16)	-0 0231(17)	-0.0317(18)
C13	0 098(3)	0 0602(18)	0.0653(19)	0.0034(15)	-0.0211(17)	-0.0028(17)
O1	0.0825(15)	0.0459(11)	0.0656(12)	0.0044(9)	-0.0252(11)	-0.0196(10)
O2	0.1004(17)	0.0478(12)	0.0900(15)	-0.0001(10)	-0.0375(13)	-0.0093(11)
O3	0.0733(13)	0.0515(10)	0.0460(9)	-0.0037(8)	-0.0152(8)	-0.0263(9)
O4	0.0778(14)	0.0628(12)	0.0561(11)	-0.0018(9)	-0.0129(10)	-0.0078(10)

deviation is observed in the C2-C3 bond length of 1.430(4)Å which higher than the normal C2-C3 bond length of coumarin (1.375(4))Å. The higher bond length of C3'-C11 keeps the CH_3 and C3-H repulsion to the minimum.

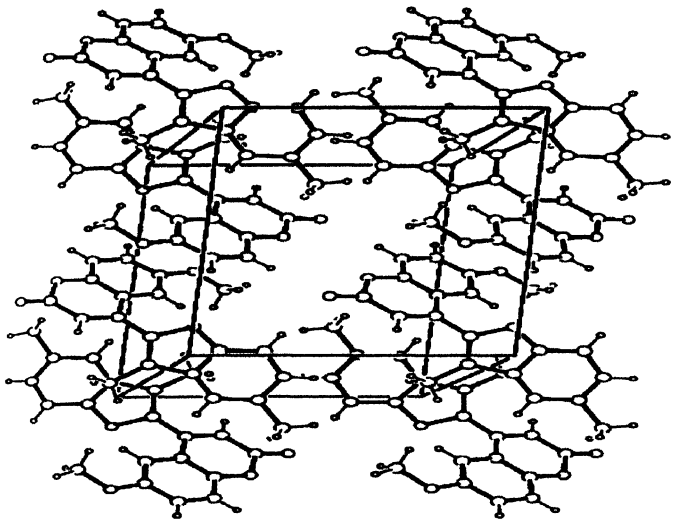

Figure 2. Packing diagram of the molecule down 'a' axis

Majority of the bond angles around sp^2 and sp^3 carbons are in the normal range of 119-122° and 109-110° respectively. However, some significant deviations have been observed. The higher values around C4'-C9'-C3' (134.5(2)°) and 128.5(2)° around C11-C3'-C2' keep the electronic repulsion to the minimum.

The benzene ring of the two coumarins are in close spatial proximity with opposite orientations. Probably, the intermolecular associations of the methoxy oxygen and the C7-H is an important force of stabilization through O...H-C bonding. The methyl group at C5' on benzofuran is stabilized by intermolecular association with the lactone oxygen. The benzofuran moieties of the two molecules are intercalating and are stabilized by Van der waals forces. These are the two important features of the molecular packing which are common all the orientations of the molecule.

The total molecule of two rings adopts a non-planar arrangement. The benzofuran ring is at an angle of 40° with respect to the coumarin ring. The C3'-methyl group of benzofuran is in spatial proximity to the C3-H of coumarin which is in agreement with the NMR (1D difference NOE) results. Further the oxygen of the benzofuran moiety is oriented towards the benzene portion of the coumarin which is also reflected in the slight deshielding of C5-H of coumarin.

The non-planarity is also reflected in the two dihedral angles around the bridging atoms C4-C2'. The C3-C4-C2'-O3 dihedral angle shows the absence of anti-periplanar relation with a dihedral angle of -141.7(3)°. The C3-C4-C2'-C3' dihedral angle is -137.8(3)° which shows the gauche relationships of the two rings.

Table 4. Selected bond lengths (Å) and bond angles (°).

Bond lengths

Atom	Bond length	Atom	Bond length
C9- C10	1.381(4)	C9- O1	1 386(3)
C9- C8	1 389(4)	C8- C7	1.375(4)
C7- C6	1.382(4)	C6- O4	1.374(4)
C6- C5	1.381(4)	C5- C10	1 415(4)
C10- C4	1.465(4)	C4- C3	1.353(4)
C4- C2'	1.459(4)	C3- C2	1 430(4)
C2- O2	1 223(3)	C2- O1	1 365(4)
C2'- C3'	1 359(4)	C2'- O3	1.392(3)
C8'- O3	1 371(3)	C8'- C7'	1 380(4)
C8'- C9'	1 382(3)	C7'- C6'	1 376(4)
C6'- C5'	1 407(4)	C5'- C4'	1 375(4)
C5'- C12	1 517(4)	C4'- C9'	1.398(3)
C9'- C3'	1 437(3)	C3'- C11	1.502(3)
C13- O4	1 419(4)		

Bond angles

Atom	Angle	Atom	Angle
C10- C9- O1	121 6(2)	C10- C9- C8	122 4(3)
O1- C9- C8	116 0(2)	C7- C8- C9	119.0(3)
C2- C3- C4	120.4(3)	O4- C6- C5	124.3(2)
O4- C6- C7	115 4(2)	C5- C6- C7	120.3(3)
C6- C5- C10	120.4(2)	C9- C10- C5	117 3(2)
C9- C10- C4	118 0(2)	C5 C10- C4	124 6(2)
C3- C4- C2'	119 4(2)	C3- C4- C10	118 3(2)
C2'- C4- C10	122 3(2)	C4- C3- C2	122 7(3)
O2- C2- O1	117.2(3)	O2- C2- C3	125.0(3)
O1- C9- C8	117 8(2)	C3'- C2'- O3	111 7(2)
C3'- C2'- C4	132 4(2)	O3- C2'- C4	115 9(2)
O3- C8'- C7'	125.5(2)	O3- C8'- C9'	110 7(2)
C7'- C8'- C9'	123 7(2)	C6'- C7'- C8'	115 9(2)
C7'- C6'- C5'	122.9(2)	C4'- C5'- C6'	119.2(2)
C4'- C5'- C12	121 5(3)	C6'- C5'- C12	119.3(3)
C5'- C4'- C9'	119.4(2)	C8'- C9'- C4'	118.9(2)
C8'- C9'- C3'	106.5(2)	C4'- C9'- C3'	134.5(2)
C2'- C3'- C9'	105.7(2)	C2'- C3'- C11	128 5(2)
C9'- C3'- C11	125.7(2)	C8'- O3- C2'	105.36(18)
C6- O4- C13	117.2(2)		

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